



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



Publication number: **0 485 985 A1**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **91119351.4**

(51) Int. Cl.<sup>5</sup>: **C07F 7/18**

(22) Date of filing: **13.11.91**

(30) Priority: **15.11.90 JP 309977/90**

(43) Date of publication of application:  
**20.05.92 Bulletin 92/21**

(84) Designated Contracting States:  
**DE FR GB**

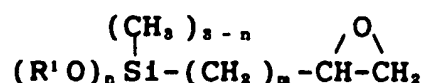
(71) Applicant: **SHIN-ETSU CHEMICAL CO., LTD.**  
**6-1, Ohtemachi 2-chome**  
**Chiyoda-ku Tokyo(JP)**

(72) Inventor: **Yamaya, Masaaki**  
**787-2, Yanase**  
**Annaka-shi, Gunma-ken(JP)**  
Inventor: **Yanagisawa, Hideyoshi**  
**21-1, Kokuga, Matsuidamachi**  
**Usui-gun, Gunma-ken(JP)**  
Inventor: **Yamazaki, Toshio**  
**791-4, Yanase**  
**Annaka-shi, Gunma-ken(JP)**

(74) Representative: **Hansen, Bernd, Dr.**  
**Dipl.-Chem. et al**  
**Hoffmann, Eitle & Partner Patent- und**  
**Rechtsanwälte Arabellastrasse 4 Postfach**  
**81 04 20**  
**W-8000 München 81(DE)**

(54) **Organosilicon compounds and methods of manufacturing thereof.**

(57) A novel organosilicon compound represented by the general formula:



(wherein R<sup>1</sup> is a monovalent hydrocarbon group having 1 to 4 carbon atoms, m is an integer of 4 to 12, and n is an integer of 1 to 3), which is useful as additives for surface treating agents such as primer, bonding agents, and paint; and to the manufacture of composite materials such as laminated boards, FRP, FRTP, resin sealants, and the molding materials.

## BACKGROUND OF THE INVENTION

The present invention relates to a novel silane compound which is useful as surface treating agents or additives, and a method of manufacturing the same. More particularly, it relates to an alkoxysilane that has an alkyl group containing 4 to 12 carbon atoms in which the terminal hydrogen atom is replaced by an epoxy group and a method of manufacturing the same.

Various methods have been employed in the past for the synthesis of a wide variety of silane compounds that have an epoxy functional group. Examples that can be found in publications include a method of using a peracid to render the terminal unsaturated double bond of an olefinic functional silane into an epoxide (see Japanese Patent Kokoku Publication No. 35-6376); and a method of utilizing a hydrosilation reaction between a hydrosilane that contains a Si-H bond and an epoxy compound that has both an epoxy group and an unsaturated double bond (see Japanese Patent Kokoku Publication No. 38-16879 and Japanese Patent Laid-Open Publication No. 62-83342).

Among the synthetic silane compounds containing an epoxy functional group are silane compounds that are produced by a hydrosilation of allylglycidyl ether, vinyl cyclohexene epoxide, or terpene epoxide.

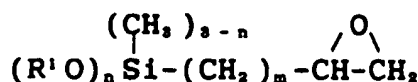
However, there has been no alkoxysilane containing a straight-chain alkyl group having four or more carbon atoms, in which the terminal hydrogen atom is replaced by an epoxy group.

## SUMMARY OF THE INVENTION

It is therefore an object of the present invention to provide an alkoxysilane containing a straight-chain alkyl group having four or more carbon atoms, in which the terminal hydrogen atom is replaced by an epoxy group, and to provide a method of manufacturing the same.

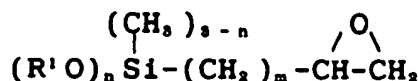
The inventors of present invention intensively studied methods of manufacturing the silane compounds described above, and have discovered that the novel silane compounds can be obtained in high yields by reacting, under the presence of a transition metal compound, a compound containing a straight-chain alkene having 4 to 12 carbon atoms, in which one terminal is a double bond and in which the hydrogen atom attached to the other terminal is replaced by an epoxy group with an alkoxysilane (in which the alkoxy group has 1 to 4 carbon atoms) containing a Si-H group. With this discovery, we were able to accomplish the present invention.

The organosilicon compound of the present invention comprises an organosilicon compound represented by the following general formula:

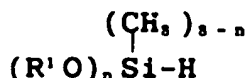


wherein R<sup>1</sup> is a monovalent hydrocarbon group having 1 to 4 carbon atoms, m is an integer of 4 to 12, and n is an integer of 1 to 3.)

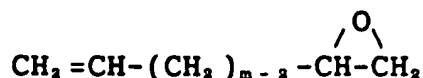
The method of manufacturing of the present invention is a method of manufacturing an organosilicon compound represented by the following general formula:



wherein R<sup>1</sup>, m, and n have the same meanings as those defined above; comprising reacting, under the presence of a transition metal compound, an organosilicon compound A represented by the general formula:



wherein R<sup>1</sup> is a monovalent hydrocarbon group having 1 to 4 carbon atoms, and n is an integer of 1 to 3 with an epoxy compound B represented by the general formula:



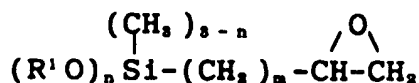
wherein m is an integer of 4 to 12.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows the <sup>1</sup>H-NMR spectra of the organosilicon compound obtained in Example 1 of the present invention. Figure 2 is the IR spectra of the same compound.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The organosilicon compound of the present invention can be represented by the following general formula, as noted in the above:



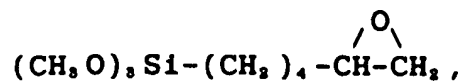
In the above formula, R<sup>1</sup> is a monovalent hydrocarbon group having 1 to 4 carbon atoms, and the specific examples of R<sup>1</sup> are listed below:

CH<sub>3</sub>-, CH<sub>3</sub>CH<sub>2</sub>-, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>-, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-,

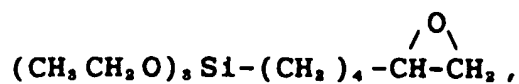


In the above formula, m is an integer of 4 to 12, and n is an integer of 1 to 3.

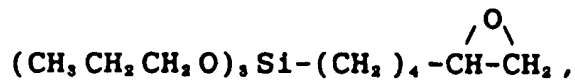
Specific examples of the organosilicon compound of the present invention are listed below:



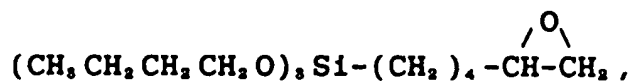
5



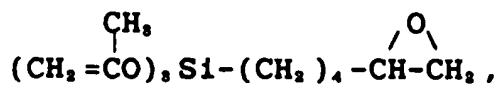
10



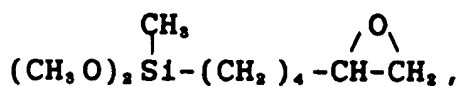
15



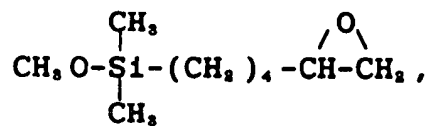
20



25



30



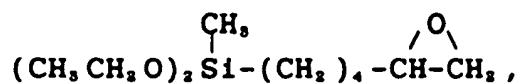
35

40

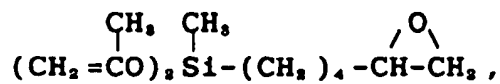
45

50

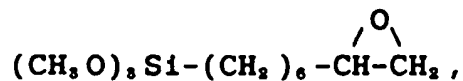
55



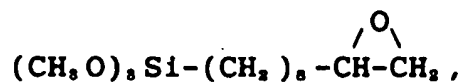
5



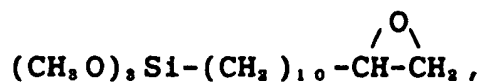
10



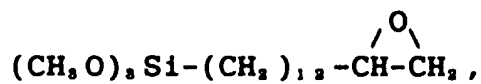
15



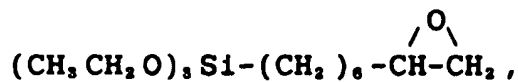
20



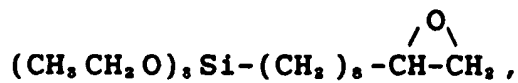
25



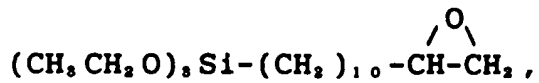
30



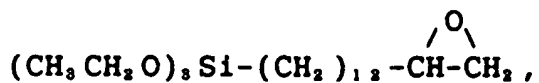
35



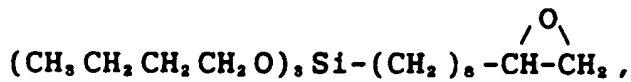
40



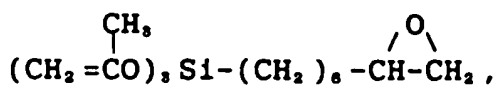
45

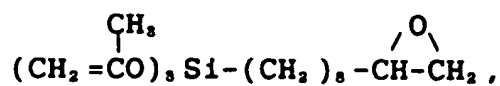


50

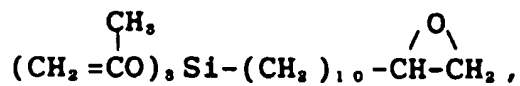


55

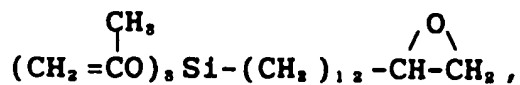




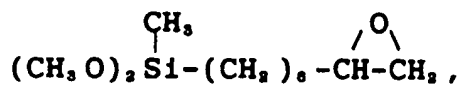
5



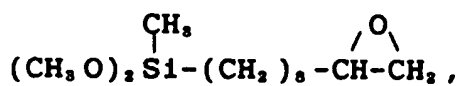
10



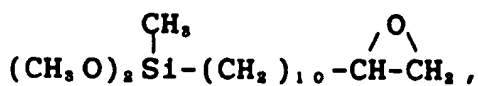
15



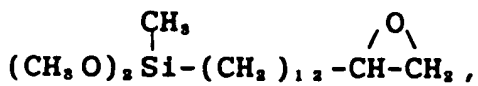
20



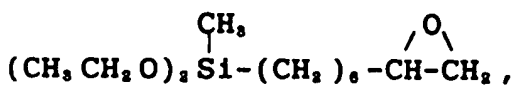
25



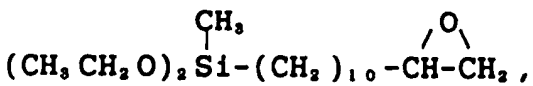
30



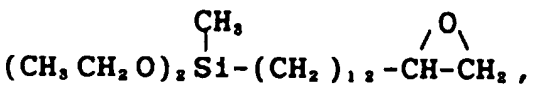
35



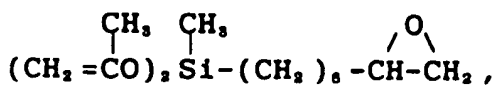
40



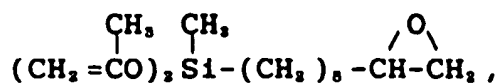
45



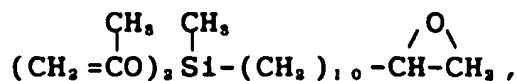
50



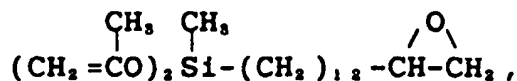
55



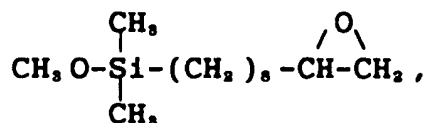
5



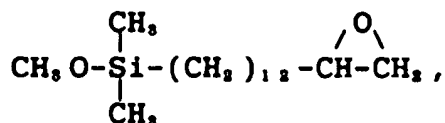
10



15



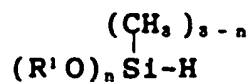
20



25

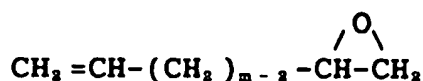
The above compounds of the present invention are manufactured by reacting, under the presence of a transition metal compound, an organosilicon compound A represented by the general formula:

30



wherein R<sup>1</sup> and n are as defined above, with an epoxy compound B, containing a double bond at one of the terminal, represented by the general formula:

35



40

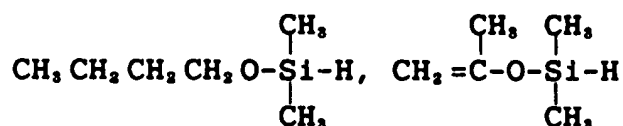
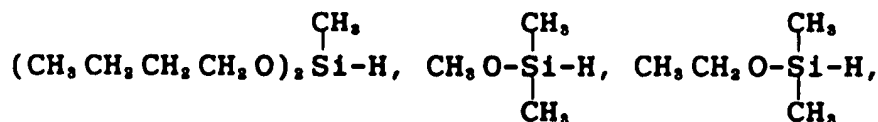
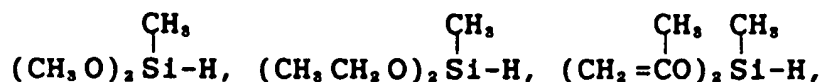
wherein m is as defined above.

Specific examples of the compound A include the following:

45 (CH<sub>3</sub>O)<sub>3</sub>Si-H, (CH<sub>3</sub>CH<sub>2</sub>O)<sub>3</sub>Si-H, (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>Si-H,

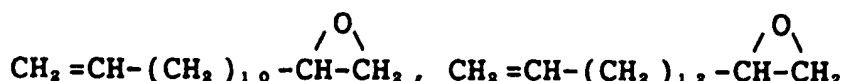
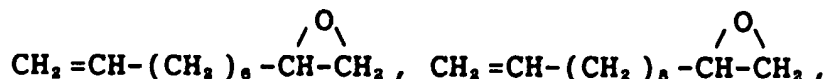
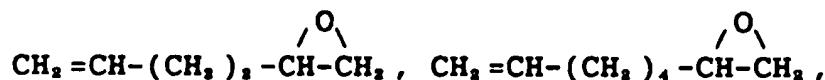
50

55



The compound B can be obtained by mono-epoxidation of a double-terminal diolefin, carried out through the use of peracetic acid or hydrogen peroxide etc. The double-terminal diolefin can be obtained by a metathesis reaction of an olefin through the use of a transition metal catalyst, such as one containing tungsten or ruthenium.

Specific examples of the compound B are listed below:



The transition metal compound used in the present invention is a reaction catalyst, and any of the known hydrosilation catalysts can be used. Preferable ones are compounds containing platinum, rhodium, ruthenium, or cobalt. These transition metal compounds can be used in the solid state, or they can be dissolved in a solvent, such as alcohols, aromatic compounds, or halogenated hydrocarbons.

Preferably, the following reaction conditions should be employed: mole ratio (the compound A / the compound B): in the range of 0.1 - 5.0; temperature: in the range of 30 - 150 °C; and reaction time: in the range of 0.5 - 20 hour. In these reaction conditions, a mole ratio of less than 0.1 or greater than 5.0 leads to a substantial decrease in pot yield and a cost increase of the final product. The more preferable range of the mole ratio is 0.3 to 3.0.

Any of the following solvents can be used for the reaction: an aromatic solvent, such as toluene and xylene; an ether solvent, such as dioxane, THF, and dibutyl ether; and an ester solvent, such as ethylacetate and butylacetate.

A useful protocol for carrying out the reaction involves placing the compound A and a transition metal compound in a reaction vessel, and allowing the compound B to drip onto it. Conversely, it is also possible to place the compound B and a transition metal compound in a reaction vessel, and allow the compound A to drip onto it.



The organosilicon compound of the present invention exhibits unique properties due to the high value of  $m$  in the above general formula, and they are suitable for applications including additives for surface treating agents such as primer, bonding agents, and paints; and for the manufacture of composite materials such as laminated boards, FRP, FRTP, resin sealants, and molding materials.

The present invention will now be described in more detail, with reference to the following examples.

#### Example 1

98g of 5,6-epoxy-1-hexene (1.0 mole) and 0.52g ( $1.0 \times 10^{-5}$  moles) of butanol solution containing 1% chloroplatinic acid were placed in a 1-L flask, under nitrogen gas, equipped with a Dimroth condenser, a thermometer, a dropping funnel, and a nitrogen gas inlet tube. After the temperature of the mixture was raised to  $60^\circ\text{C}$ , 116g (0.95 mole) of trimethoxysilane were allowed to slowly drip onto the mixture. After the temperature was maintained at  $60^\circ\text{C}$  for three hours, the mixture was distilled under a 2-Torr condition at a  $100^\circ\text{C}$  boiling point. The result was 169g of a clear, colorless liquid. Subsequent  $^1\text{H-NMR}$ , IR, and elemental analyses confirmed that the liquid has the following structural formula:



The yield of the product was 77%. Its purity, as determined by gas chromatography, was 98.7%. Further, the product exhibited the following physical properties: viscosity, 2.36 cs; specific gravity, 1.024; and refractive index, 1.4243.

$^1\text{H-NMR}$  analysis (Figure 1; internal standard: benzene) Chemical shift ( $\delta$ ):

3.53ppm(s, 9H) :  $(\text{CH}_3\text{O})_3\text{Si}-$

2.6 ~ 2.9ppm (m, 1H) :  $-\text{CH}-\text{CH}_2$

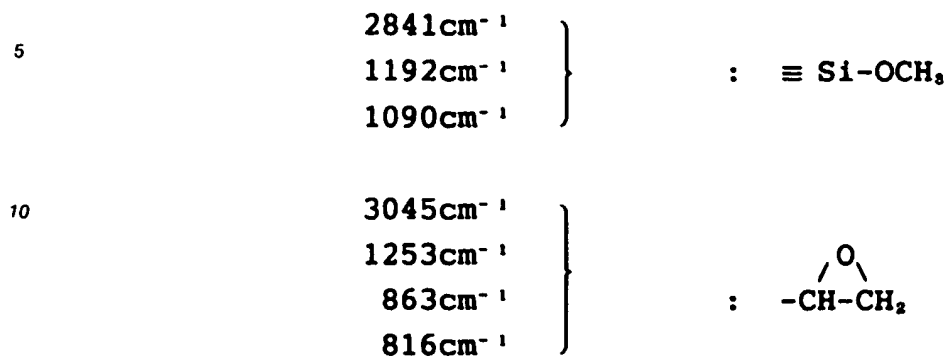
2.58ppm(t, 1H) :  $\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}-\text{C} \\ \diagup \quad \diagdown \\ \quad \text{H} \end{array}$

2.37ppm(double-d, 1H) :  $\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}-\text{C} \\ \diagup \quad \diagdown \\ \quad \text{H} \end{array}$

1.2 ~ 1.7ppm (m, 6H) :  $\equiv \text{Si}-\text{CH}_2-(\text{CH}_2)_3-\text{CH}-\text{CH}_2$

0.4 ~ 0.85ppm (broad-t, 2H) :  $\equiv \text{Si}-\text{CH}_2-(\text{CH}_2)_3-$

IR analysis (Figure 2):



Elemental analysis:

20

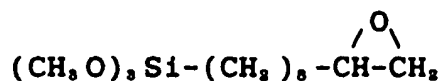
	Theoretical value (%)	Observed value (%)
C	48.62	48.45
H	9.07	9.24
Si	12.63	12.51

25

## Example 2

30        A reaction was carried out under the same conditions as those described in Example 1, except that 154g (1.0 mole) of 9,10-epoxy-1-decene was used in lieu of 5,6-epoxy-1-hexene. A distillation performed under conditions of 132 °C boiling point and 2 Torr after the reaction period yielded 138g of a reaction product. Subsequent <sup>1</sup>H-NMR, IR, and elemental analyses confirmed that the product has the following structural formula:

35



45        The yield of the product was 50%. Its purity, as determined by gas chromatography, was 98.0%. Further, the product exhibited the following physical properties: viscosity, 4.56 cs; specific gravity, 0.978; and refractive index, 1.4336.

50

55


### <sup>1</sup>H-NMR analysis

Chemical shift ( $\delta$ ):

5 3.52ppm(S, 9H) : (CH<sub>3</sub>O)<sub>3</sub>Si-

2.6 ~ 2.9ppm (m, 1H) :  $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ -\text{CH}-\text{CH}_2 \end{array}$

2.60ppm(t, 1H) : 

2.38ppm(double-d, 1H) : 


25 1.2 ~ 1.7ppm (m, 14H) :  $\equiv \text{Si}-\text{CH}_2-(\text{CH}_2)_7-\overset{\text{O}}{\text{CH}}-\text{CH}_2$

0.4 ~ 0.8ppm (broad-t, 2H) :  $\equiv$  Si-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>7</sub>-

30 IR analysis (Figure 2):

35  $\left. \begin{array}{l} 2842\text{cm}^{-1} \\ 1191\text{cm}^{-1} \\ 1090\text{cm}^{-1} \end{array} \right\} : \equiv \text{Si-OCH}_3$

40

3045cm <sup>-1</sup>	}	:	
1253cm <sup>-1</sup>			
863cm <sup>-1</sup>			
814cm <sup>-1</sup>			

45

Elemental analysis:

50		Theoretical value (%)	Observed value (%)
	C	56.08	55.82
	H	10.14	10.33
	Si	10.09	10.01

## Example 3

A reaction was carried out under the same conditions as those described in Example 1, except that 127.3g (0.95 mole) of methyldiethoxy silane were used in lieu of trimethoxysilane. A distillation performed under conditions of 78°C boiling point and 2 Torr after the reaction period yielded 174g of a reaction product. Subsequent <sup>1</sup>H-NMR, IR, and elemental analyses confirmed that the product has the following structural formula:



The yield of the product was 75%. Its purity, as determined by gas chromatography, was 98.3%.

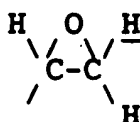
<sup>1</sup>H-NMR analysis

Chemical shift (δ):

3.76ppm(q, 4H) : ≡ Si-O-CH<sub>2</sub>CH<sub>3</sub>

2.6 ~ 2.9ppm (m, 1H) : -CH-CH<sub>2</sub>

2.60ppm(t, 1H) : 

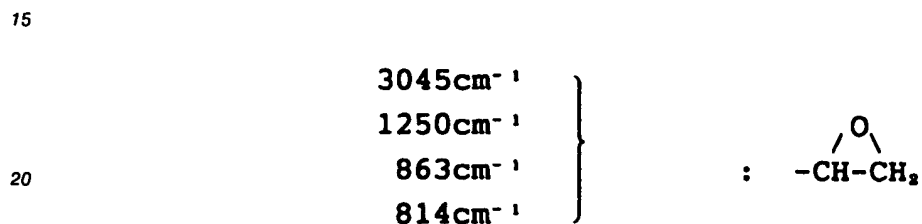
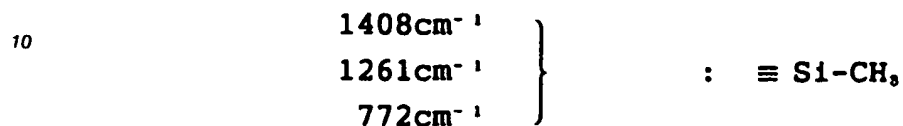
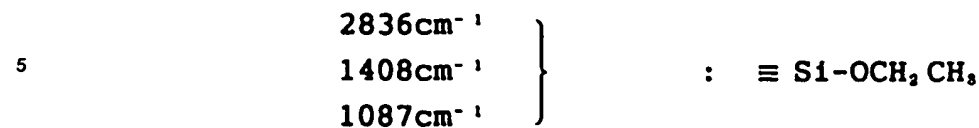
2.38ppm(double-d, 1H) : 

1.2 ~ 1.7ppm (m, 6H) : ≡ Si-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>3</sub>-CH-CH<sub>2</sub>

1.18ppm (t, 6H) : ≡ Si-O-CH<sub>2</sub>CH<sub>3</sub>

0.05ppm (s, 3H) : ≡ Si-CH<sub>3</sub>

## IR analysis



## 25 Elemental analysis:

	Theoretical value (%)	Observed value (%)
30 C	56.85	56.74
H	10.41	10.58
Si	12.09	12.00

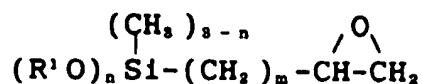
## 35 Claims

1. An organosilicon compound represented by the following general formula:

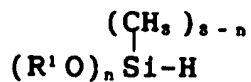


45                      wherein  $\text{R}^1$  is a monovalent hydrocarbon group having 1 to 4 carbon atoms,  $m$  is an integer of 4 to 12, and  $n$  is an integer of 1 to 3.

2. The organosilicon compound of claim 1, wherein the  $\text{R}^1$  is methyl group.
3. The organosilicon compound of claim 1, wherein the  $\text{R}^1$  is ethyl group.
- 50 4. The organosilicon compound of claim 2 or 3, wherein  $m$  is 4; and  $n$  is 3.
5. The organosilicon compound of claim 2 or 3, wherein  $m$  is 8; and  $n$  is 3.
- 55 6. A method of manufacturing an organosilicon compound represented by the following general formula:



wherein R<sup>1</sup> is a monovalent hydrocarbon group having 1 to 4 carbon atoms, m is an integer of 4 to 12, and n is an integer of 1 to 3, which comprising reacting, under the presence of a transition metal compound, an organosilicon compound A represented by the general formula:



wherein R<sup>1</sup> is a monovalent hydrocarbon group having 1 to 4 carbon atoms, and n is an integer of 1 to 3 with an epoxy compound B represented by the general formula:



wherein m is an integer of 4 to 12.

7. The method of claim 6, wherein the mole ratio between the organosilicon compound A and the epoxy compound B to be reacted is in the range of 0.1 to 5.0.
8. The method of claim 6, wherein the mole ratio between the organosilicon compound A and the epoxy compound B to be reacted is in the range of 0.3 to 3.0.
9. The method of claim 6, wherein the organosilicon compound A is trimethoxysilane or methyldiethoxysilane.
10. The method of claim 6, wherein the organosilicon compound B is 5,6-epoxy-1-hexene or 9,10-epoxy-1-decene.

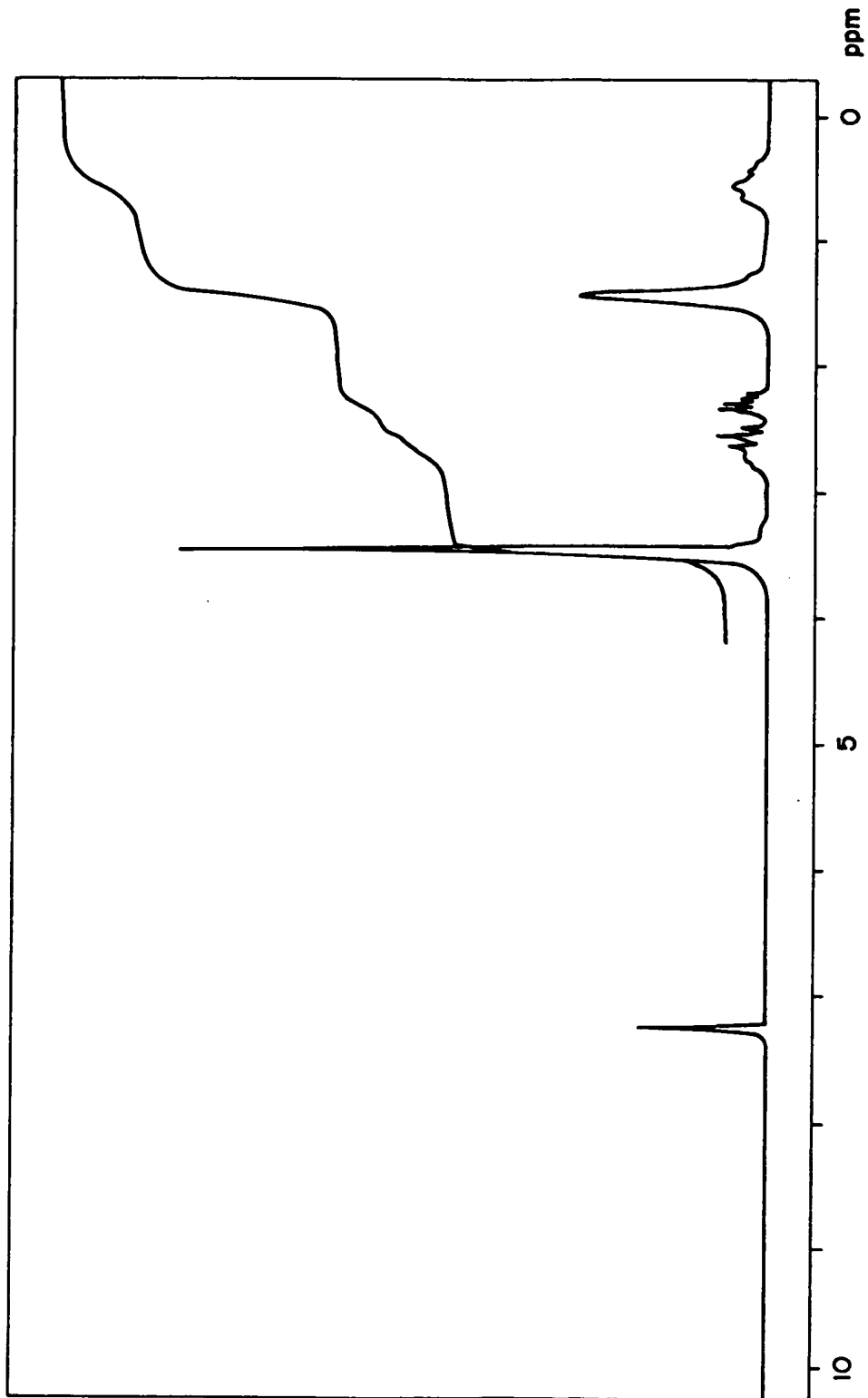
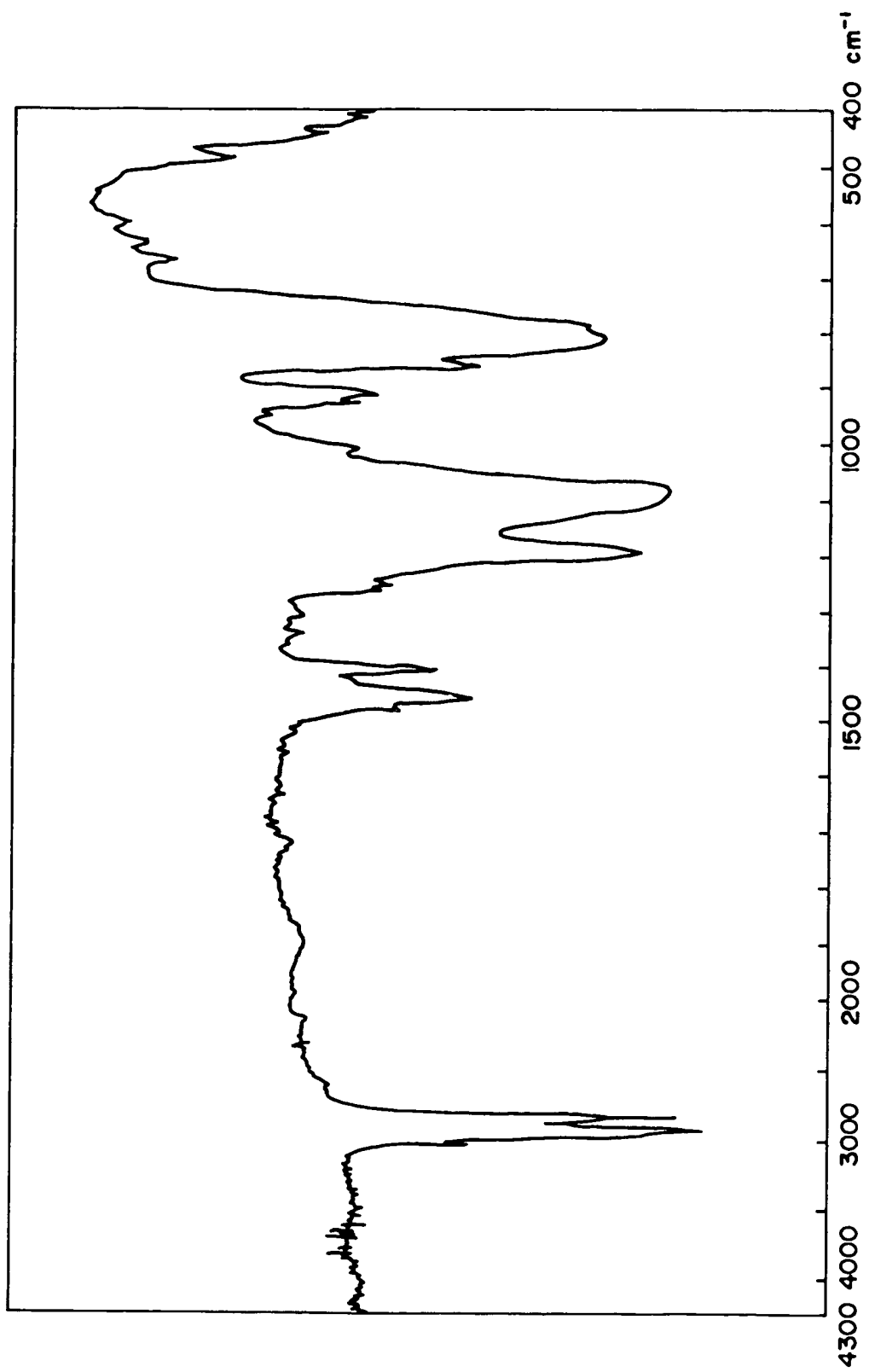
*FIG. 1*

FIG. 2







European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 91 11 9351

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	JP-A-0 245 758 (JAPAN CHEMICALS INSPECTION AND TESTING INSTITUTE) * the whole document * ---	1-10	C07F7/18
X	JP-A-63 264 174 (DAINIPPON INK AND CHEMICALS, INC.) * the whole document * ---	1-10	
X	JP-A-6 149 306 (TORAY INDUSTRIES, INC.) * the whole document * ---	1-10	
X	US-A-4 990 549 (DELVIN, A.M. ET AL) * the whole document * ---	1-10	
X	JP-A-59 120 672 (KANEKAFUCHI CHEMICAL INDUSTRY CO., LTD.) * the whole document * ---	1-10	
X	US-A-3 619 256 (PEPE, A.E. ET AL) * the whole document * ---	1-10	
X	FR-A-1 548 971 (GENERAL ELECTRIC COMPANY) * the whole document * ---	1-10	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
X	EP-A-0 217 236 (PCR, INC.) * the whole document * ---	1-10	C07F
X	EP-A-0 288 286 (TOA NENRYO KOGYO KABUSHIKI KAISHA) * the whole document * ---	6-10	
A	* the whole document * ---	1-5	
X	EP-A-0 262 642 (UNION CARBIDE CORPORATION) * the whole document * ---	6-10	
A	* the whole document * -----	1-5	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 07 FEBRUARY 1992	Examiner RINKEL L. J.
<b>CATEGORY OF CITED DOCUMENTS</b> X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document			